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Chemistry. -- "Influence of different compounds on the destruction of monosaccharids by sodiumhydroxide and on the inversion of sucrose by hydrochloric acid II". By Dr. H. I. WATERMAN. (Communicated by Prof. J. BOESEKEN).

(Communicated in the meeting of June 30, 1917).

In a previous communication¹) it has been proved that in alkalic solutions amino acetic acid and α amino propionic acid behave about as one-basic acids, because they retard the destruction of glucose by alkali almost as much as an equivalent quantity of hydrochloric acid.

In acidic solution the said amino acids act about as monacidic alkali since they retard the inversion of sucrose by hydrochloric acid almost in an equal degree as the equivalent quantity of strong alkali.

It could be expected that other amino-acids with a greater number of atoms of carbon should in the same way show in alkalic solution ' strong acidic, in acidic solution strong basic properties as well. Experiment has confirmed this expectation.

The following α -aminoacids were examined:

Behaviour in alkalic solution.

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The just mentioned aminoacids prevent the destruction of glucose by sodiumhydroxide as is proved by the following. A solution of 50 Gr. glucose in distilled water after being boiled was diluted to 1 Liter.

1) Chemisch Weekblad, 14, 119 (1917). These Proceedings, Vol. XX, p. 88, April 27, 1917.

From this solution 40 cm³. was taken with a pipette. I let it flow into a 50 cm³. flask, added a fixed quantity of the aminoacid in question to some of the flasks and added at the same time different volumes of a solution of sodium hydroxide of known strength.

Finally the liquids were diluted with H.O to 50 cm³. and shaken thoroughly. The thus obtained solutions were placed in a thermostat with waterjacket (temperature 34°), the temperature of the liquid in the flasks therefore rising gradually. At the beginning of the experiment and later from time to time the polarisation and the intensity of colour of the solutions were determined under comparable circumstances. The results of these observations are found in table I. (See table on the following page).

From the results mentioned in this table it follows in the first place that the aminoacids in question practically do not influence the polarisation of glucose (polarisation of Nrs. 6, 7 and 8 at beginning).

After $3^{1}/_{2}$ hours the polarisation has diminished most in the flasks that contained the largest quantity of NaOH (Nrs. 5 and $9: +4^{\circ}$, 6 V.).

Although the added number of cm³, of the NaOH-solution with the Nrs. 6, 7 and 8 is equally great as that with the Nrs. 5 and 9,it follows from the table that the polarisation with 6, 7, and 8 has diminished only to respectively 6,5, 6,6, and 6,5.

This number is less than that of N^0 . 3 to which 3 cm³. of the NaOH-solution had been added. We may therefore conclude that two milligram molecules of each of the aminoacids compensate the action of about 2 cm³. of 1,06 normal NaOH-solution. The intensity of colour too of Nrs. 6, 7, and 8 (after $+21$ and 6×24 hours) that lies between that of Nrs. 3 and 4 was herewith in agreement.

The *a*-aminocompounds of butyric acid, isovaleric acid and isocaproic acid therefore behave in alkalic solution as about monobasic acid.

Behaviour in acidic solution.

The inversion of sucrose by hydrochloric acid was likewise prevented by the said three α -aminoacids.

From the results united in table Πa and Πb especially from the polarisation at the beginning of the experiments it follows that these three aminoacids neither influence to an important degree the polarisation of sucrose nor change polarisation of the solution by their own optical activity.

Whilst the polarisation after addition of 5 cm³ 1,01 normal hydrochloric acid after $16\frac{1}{3}$ hours (Table II^a) has lowered to respectively

TABLE I.

N ₀		Added	Number of cm ³ 1,06 Norm.NaOH- sol. added		Polarisation in grades VEN1ZKE (2 dm. tube)		Colour of the solution	
					At begin- nıng of thel experi- ment 1)	After $\pm 3\frac{1}{2}$ hours	After $+$ 21 hours	After \pm 6×24 hours
$\mathbf{1}$	40 cm^3 . of a sol. containing glucose (50 Gr. gluc.to 1 Liter)		$\bf{0}$	34°) thermostat with watermantle (Temp.	$+11,5$	$+11,4$	colour- less	colour- less
$\overline{\mathbf{2}}$	id.		$\overline{\mathbf{c}}$		2)	$+8,1$	pale yellow	pale yellow
3	ıd.		3		2)	$+6,8$	yellow	yellow
$\overline{\mathbf{4}}$	1d.		4		2)	$+5,6$	vellow brown	brown- yellow
5	id.		5 _l		$+10,0$	$+4,6$	deep yellow- brown	deep brown
6	id.	206 milligram s-aminobutyric acid (= 2 milli grammolecule)	5	placed in	$+10,5$	$+6,5$	yellow, somewhat deeper than Nº. 3	brown-yellow, paler than Nº. 4
$\overline{1}$	id.	234 milligram <i>z</i> -aminoisova- leric acid $(= 2)$ mgr. molecule	, 5	$cm3$ and	$+10,7$	$+$ 6,6		
8	id.	262 milligram z-aminoisoca- proic acid $(=2$ mgr. mol.).	5	50 S, ę	$+10,6$	$+6,5$		
9	id.		$\mathbf{5}$	Filled	$+10,3$	$+4,6$	deeper yellow- brown	deeper. brown

Influence of σ aminobutyric acid, x-aminoisovaleric acid and σ -aminoisocaproic acid on the destruction of glucose by alkali.

 $+1,2$ and $+2,5$ (Nrs. 4 and 7) the addition of 2 milligrammolecules of α -aminobutyric acid and α -aminoisovaleric acid causes that in presence of the same quantity of hydrochloric acid the polarisation has diminished only to respectively $+12.2$ and $+11.9$ (Nrs. 5 and 6). From this results that the added quantities of these amino acids

¹) Between the dilution to 50 cm⁵ and the determination of polarisation of course some 'time passes.

²) The polarisation was not determined; the results obtained would lie hetween that of N^0 . 1 (+11,5) and those of Nrs. 5 and 9 + (10,0 and + 10,3) and would diminish gradually from N^0 . 2 to N^0 . 4 (Compare the results obtained before).

compensate the action of somewhat less than 2 cm³ of normal hydrochloric acid, which is demonstrated too by the observations made after $24, 40-41$ and 72 hours.

Therefore they act about as monacidic alkali. From the observation after ± 89 hours it follows that finally the same end-situation is reached so that the stated influence of the amino acids cannot be ascribed to an accidental influence on the polarisation of fructose or glucose.

TABLE IIb.

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 $T A B L E I\dot{a}$ $\overline{1}$ Influence of s-aminobutyric acid and 'x-aminoisovaleric acid on the inversion of sucrose by hydrochloric acid.

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TABLE IIIb.

Influence of tyrosine on the destruction of glucose by alkali.

¹) This solution was boiled for a moment and afterwards cooled till the temperature of the room was reached.

²) All the glutamic acid is dissolved.

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From Table II^b it follows in an analogous way that 2 milligrammolecules of leucin (α -aminoiso-caproic acid) neutralizes the action of \pm 1¹/₂ cm³ of normal hydrochloric acid. In acidic solution leucine behaves as $\pm \frac{3}{4}$ acidic alkali.

Then I set myself to the examination of three more complicated compounds viz.

I observed that with my experiments acetamide CH_{\star} . CO (NH_a) and urea $CO(NH₂)$, behaved in alkalic and in acidic solution as practically neutral.

From this appears again a contrast between the acid amides and the amino acids: I observed before this contrast in another direction.¹)

Furthermore it has been proved in a previous communication²) that in alkalic solution phenol acts about as a one-basic acid, whilst this compound practically has no influence on the inversion of sucrose by hydrochloric acid.

In agreement with these results it could be expected that in alkalic solution asparagine possessing the carboxyl group should behave as a one basic acid. For the presence of the amino group asparagine should behave as monacidic alkali in acidic solutions.

Glutamic acid, which compound possesses two carboxyl-groups in presence of sodium hydroxide should act as a two-basic acid; in acidic solution it should behave as monacidic alkali (NH₃-group). Finally tyrosine for the presence of the phenolic hydroxyl-group and the carboxyl-group in alkalic solution should be two basic acid; in acidic solution the (NH₂) group should render it monacidic alkali. These predictions were confirmed by the experiments (Table III^a, III^b and IV).

From the experiments mentioned in Table III^a it follows that under the circumstances described asparagine acts as monobasic acid.

1,06 milligrammolecule of asparagine neutralizes the action of about 1 cm³ 1,06 normal NaOH-solution, as results from the polarisation after $3\frac{1}{4}$ hours.

1) H. I. WATERMAN, Die Stickstoffnahrung der Presshefe, Folia microbiologica. (Holländische Beiträge zur gesamten Mikrobiologie) 2, 173 (1913).

²) These Proceedings, Vol. XX, 88 (April 27, 1917).

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TABLE IV. Influence of asparagine, tyrosine and glutamic acid on the inversion of sucrose by hydrochloric acid.

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 $\mathcal{L}_{\mathbf{X}}$, where $\mathcal{L}_{\mathbf{X}}$

 \mathcal{L}_{max}

 $\mathcal{L}_{\mathcal{A}}$

 $\overline{1}$

¹) All the glutamic acid is dissolved.

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Much stronger is the defending influence of 1,06 milligrammolecule glutamic acid and of 1,06 milligrammolecule tyrosine, which compensate the action of about 2 cm³ 1,06 normal NaOHsolution (polarisation after $3^{1}/_{2}$ hours).

Glutamic acid acts just like tyrosine as almost two basic acid, which was once more confirmed for the latter compound by the experiment described in table IIIb.

It must be remarked that the glutamic acid $(N^{\circ}, 7)$ did not quite dissolve even after being shaken repeatedly.

Nevertheless \pm 14 cm³ of the clear solution were used at the beginning for the determinion of polarisation.

In the remaining alkalic liquid all the glutamic acid was dissolved after some time (within $3^{1}/_{2}$ hours). The tyrosine (N°. 8, table IIIa and N° . 3, table IIIb) was dissolved but little. At the addition of the NaOH-solution after being shaken it was quite dissolved.¹)

The addition of hydrochloric acid too causes the rapid solution of tyrosine.

This compound in this regard resembles substances such as zinchydroxide and aluminiumhydroxide.

In acidic solution the glutamic acid dissolved but gradually. I did not determine polarisation before all had dissolved. Although the glutamic acid therefore could not be active to a certain extent at the beginning of the experiments, from the results obtained it can be concluded with rather great certainty that glutamic acid in acidic solution behaves as monacidic alkali.

Tyrosine too (table IV, N^0 . 6) behaves in acidic solution as monacidic alkali; 1 milligrammolecule compensates the action of about 1 cm³ of normal hydrochloric acid.

Asparagine acts as $\frac{3}{4}$ -acidic alkali; 2 milligrammolecules compensate the invertive action of about 1,5 cm³ of normal hydrochloric acid (Table IV, N° . 5).

Afterwards aniline and pyridine were subjected to research, in how far these compounds influence the destruction of glucose by alkali and the inversion of sucrose by hydrochloric acid.

1) In heating the solution to the boiling point but without the addition of NaOH the tyrosine dissolved almost quite, but in cooling till the ordinary temperature was reached an important quantity crystallised, which was dissolved rapidly at the addition of NaOH.

The aniline present in the laboratory was distilled with steam and after drying distilled in the ordinary way. The boiling point was 180°.

The pyridine of the laboratory was distilled in fractions. The fraction which boiled between 115° and 117° was used for the research.

It could be expected that in alkalic solution both compounds should behave neutral, in acidic solution they should act as monacidic base.

The referential experiments which are mentioned in table V and VI have confirmed this expectation.

Influence of aniline and pyridine on the destruction of glucose by alkali.

From table $V1a$ it follows that the retarding power of aniline on the inversion is very great.

The polarisation proves that practically no sucrose has been inverted.

1) The solution was boiled for a short time and afterwards cooled down to the ordinary temperature.

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TABLE VI. Influence of aniline and pyridine on the inversion of sucrose by hydrochloric acid.

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Herewith the fact was in agreement that after 24 hours the liquid of N° . 6 (VIa) did not possess any reducing power on FEHLING's *solution.*

A iodometrical determination of invert-sugar proved that less than 60 milligrams of invert-sugar was present per 100 cm³.

If the liquid of N° . 6 (VIa) after 24 hours is boiled for some time the reducing power on FEHLING's *solution* becomes greater. Boiling with an extra quantity of strong hydrochloric acid gives a liquid that after being neutralized with alkali possesses a strong reducing action on FEHLING's *solution*.

From table VIb it follows that 500 milligrams and 640 milligrams of aniline compensate the action of respectively \pm 5 cm³. and 7 cm³. of normal hydrochloric acid, which proves that in acidic solution aniline behaves as monoaeidic alkali.

From table $V1c$ it can further be concluded that 0.494 gr. of pyridine, compensates about 6 cm^3 . of normal hydrochloric acid, pyridine acts therefore about as monacidic alkali in acidie solution.

The basic and acidic character of the compounds described in the above is in accordance with the constitution-formula, which nowadays are assumed for these compounds.

The method of research described can help to find a better constitution-formula in cases where the said accordance does not exist \cdot).

For the rest one may be astonished a little by the strong neutralizing action against hydrochloric acid on the one hand, sodiumhydroxide on the other hand of componnds being generally known as feeble acids or basic substances.

Frequently we can make good use of this neutralizing action of substances with a but feebly acidic or basic character in watery solution in order to compensate the influence of strong alkali or strong acid.

In many experiments in the laboratory as well as in technical processes we have often to struggle with the formation of strong basic substances or strong aeids. In sueh cases we can compensate the action of the strong alkali or acid by the addition of efficient amphoter or weak electrolytes.

Dordrecht, June 1917.

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 $1)$ A first example of this was given in the preceding communication with the betain.